NASA TECHNICAL TRANSLATION

NASA TT F-13,680

THE HALL EFFECT IN POLYCRYSTALLINE SEMICONDUCTOR TEST SPECIMENS

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Translation of "Zjawisko Halla w polikrystalicznych probkach polprzewodnikowych," Archiwum Elektrotechniki, Vol. 19, No. 4, 1970, pp. 855-863.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JULY 1971

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THE HALL EFFECT IN POLYCRYSTALLINE SEMICONDUCTOR TEST SPECIMENS

A. Kobendza and M. Chorazy[1]

ABSTRACT: Description of the model of a polycrystalline semiconductor film assuming that the grains and the boundaries between them have different conductivities and Hall mobilities. The effect of grain boundaries on the measured values of conductivity, Hall mobility, and concentration of current carriers is estimated. Using this model, the relation between Hall mobility and the illumination intensity in polycrystalline cadmium selenide is determined with allowance for the production technique of semiconductor films. A71-18187

1. Introduction

The Hall effect was discovered at the end of the 19th century (in 1879). /855* Today, it is generally applied in the physics of semiconductors to determine the concentration of current carriers. In some cases, the Hall effect also furnishes information on the band structure of a semiconductor.

The classical Hall effect refers to electrically homogeneous specimens of constant thickness. However, in practice, specimens are not measured under the above conditions. Examples are specimens of evaporated semiconductors with a granular structure.

Grain sizes are considerably smaller than the linear dimensions of the entire test specimen, about 1 micron. The boundaries between them can have different electrical properties from those of the material of the neighboring grains. The question therefore often arises as to whether measurements of the Hall effect serve any useful purpose when these specimens are used. It is difficult to answer the question unequivocally.

But if an elementary, simple model of a granular specimen is used, we can provide a number of practical corollaries for the estimation of Hall measurements on vapor-deposited polycrystalline layers. The purpose of this article is to discuss this matter, with special emphasis on cadmium selenide vapor-coated layers.

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* Numbers in the margin indicate pagination in the foreign text.

2. Fundamental assumptions and conditions

Figure 1 shows a polycrystalline semiconductor specimen which we can use to measure the Hall effect.

Let us assume that only one kind of carriers, electrons, takes part in current conductance.

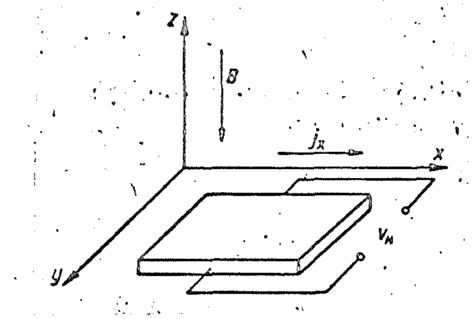

Figure 1. Specimen for Hall measurements

Current $j_x (E_x > 0)$ flows in the direction of the x axis of the specimen. /856
The induced magnetic field, B, is directed perpendicular to the surface of the specimen along axis z. The Hall voltage occurs along axis $y (j_y = 0)$.

The following units will be used:

$j_x [A/m^2]$; $x [m]$; E_x, $E_y [V/m]$; $B [T]$;

$\sigma [S/m]$; $R_H [m^3/C]$; $u_H [m^2/Vs = 1/T]$

The electric field intensity in the direction of the y axis is

$$E_y = R_H j_x B, \tag{1}$$

where $R_H = -A\frac{1}{en}$ is the Hall coefficient, constant A = 1 to 2 depending on the scattering mechanism of the carriers in the crystal lattice, and $j_x = \sigma E_x = en\mu_n E_x$.

After substituting these magnitudes in Equation (1)

$$\begin{aligned} E_y &= -A\mu_n E_x B, \\ E_y &= -\mu_H E_x B. \end{aligned} \tag{2}$$

In polycrystalline layers and intermetallic compounds A = 1.

3. Model used for a polycrystalline test specimen

The following model is taken for a test specimen of a polycrystalline semiconductor. The grains are squares, w on a side; the partitioning boundaries of the square have width h (Figure 2). Thickness of the specimen is constant and equal to d. Conductivity and mobility of grains are taken as σ_1 and μ_1; of the boundaries, as σ_2 and μ_2, respectively, and for the whole polycrystalline specimen as σ and μ_H. The magnitude of w is many times smaller than the dimensions of the specimen.

The conductivity σ of the polycrystalline specimen can be expressed by

$$\sigma=\frac{1}{\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\frac{h}{w}}+\frac{\sigma_2 h}{h+w}. \quad (3)$$

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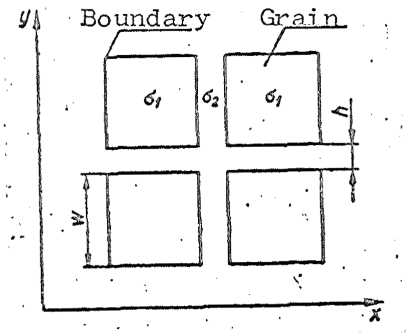

Figure 2. Model of a polycrystalline layer

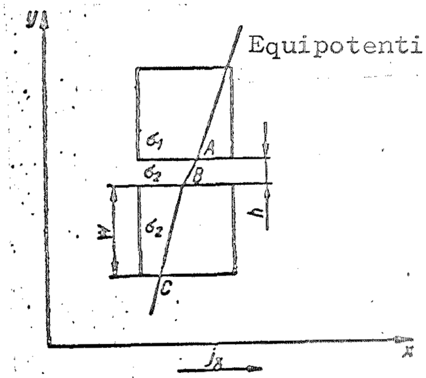

Figure 3. Model of a layer in case of boundaries parallel to the current vector.

The grain boundaries have different effects on the Hall effect, depending on whether their conductivity is larger or smaller than the grain conductivity. Moreover, their influence on the Hall effect is different depending on the angle current j_x makes with the boundary.

3.1 High-resistivity boundaries $\sigma_1 > \sigma_2$

a) The current vector j_x is parallel to the boundary

$$E_x = E_1 = E_2.$$

The electric field is constant in the grain and at the boundary, and is E_x. Currents of different densities, j_1 and j_2, flow through the grain and the boundary where $\sigma_1 \neq \sigma_2$. A bend is recorded on the equipotential line ABC at the boundary transition, where the Hall effect is different in two areas.

Let us designate the Hall voltage, V_H, between points AC (Figure 3) as

$$-V_H=\mu_1 BE_x w+\mu_2 BE_x h. \quad (4)$$

Substituting $\mu_1 = \mu_2$, we get the equation for a homogeneous specimen

$$-V_{H1}=\mu_1 BE_x(w+h), \tag{5}$$

$$\frac{V_{H1}}{V_H}=\frac{\mu_1(w+h)}{\mu_1 w+\mu_2 h}. \tag{6}$$

Eq. (6) yields the relative change in the Hall voltage caused by the existence of a high-resistance intergranular boundary parallel to the current vector.

Eq. (6) is for a single boundary and a single grain, but it is valid for a multigrain specimen.

b) <u>The current vector j_x is perpendicular to the boundary</u>

$$j_x = j_1 = j_2.$$

The current density is constant in both grain and boundary, and is j_x. The electric field depends on the conductivity of the area of grain and boundary, and is E_1 and E_2, respectively, /858

$$E_1=\frac{j_x}{\sigma_1} \quad \text{and} \quad E_2=\frac{j_x}{\sigma_2}.$$

Let us designate the Hall voltage V_H between points AC (Figure 4)

$$-V_H=\mu_2 B\frac{j_x}{\sigma_2}l+\mu_1 B\frac{j_x}{\sigma_1}S. \tag{7}$$

If $\mu_1 = \mu_2$ and $\sigma_1 = \sigma_2$ does not hold at the grain boundaries

$$-V_{H1}=\mu_1 B\frac{j_x}{\sigma_1}(l+S), \tag{8}$$

$$\frac{V_{H1}}{V_H}=\frac{\frac{\mu_1}{\sigma_1}(l+S)}{\frac{\mu_2}{\sigma_2}l+\frac{\mu_1}{\sigma_1}\cdot S} \tag{9}$$

Eq. (9) yields the relative change in the Hall voltage, V_{H1}, caused by the existence of a high-resistance intergranular boundary perpendicular to the current vector.

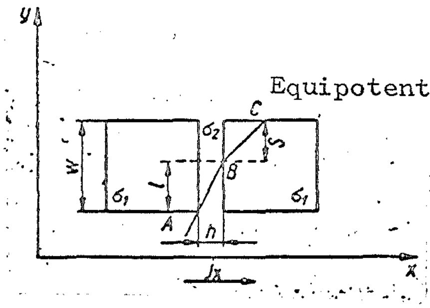

Figure 4. Model of a layer with boundaries perpendicular to the current vector

Eq. (9) depends on the magnetic field. In Eq. (2), for the Hall effect, $E_y/E_x = tg\vartheta$

$$\frac{h}{l} = \operatorname{tg}\theta \cong \theta = \mu_2 B, \tag{10}$$

$$l = \frac{h}{\mu_2 B} = f(B),$$

$$S = f(B) \text{ where } l + S = \text{const}.$$

The magnitude of l can be larger than h by many orders of magnitude, as will be seen from Eq. (10), as well as by w.

When $l > w$, Eq. (7) does have a definite error, but still can be used to estimate the change in the Hall effect produced by the boundary.

$l/(l+S) = h(w+h)$ and $S/(l+S) = w/(w+h)$ can be taken as the first approximation in the case of a real polycrystalline specimen. It expresses the fact that a part of the equipotential line passes through the grain and a part through the boundary. Accordingly, its length is proportional to w and h. /859

Eq. (10) can be omitted in the polycrystalline layers.

3.2 Boundaries are better conductors than grains, $\sigma_2 \gg \sigma_1$

The Hall effect is reduced at good conducting boundaries because the Hall voltage is shorted through the good conducting area. This phenomenon is analogous to the influence of current electrodes on the Hall voltage [1].

In the specimen of an electrode system with $l/w \geq 3$ (l - length, w - width of the specimen), the Hall effect is practically the same as for a much longer specimen ($l \to \infty$). On the other hand, when $l/w = 0.25$, voltage V_H is reduced to 20% of the previous value. The reduction in V_H is associated with the fact that the equipotential lines in the semiconductor in the vicinity of the edge of the current electrodes are not parallel to them. There are good conducting boundaries in true polycrystalline layers some of which are perpendicular to the current flow and play the role of the above-mentioned current contacts. The grain boundaries themselves can show a certain Hall effect. However, the effect will be negligible when average conductivity, and consequently the current, j_x, is low.

4. Limitations of the model used

The model of the polycrystalline-layer structure can be simplified. When current flows through the polycrystalline layer, electrical charge can accumulate at the grain boundaries, conditioned by a change in the electrical field vector, E, at the boundary of the two media. Moreover, the change in the carrier concentration changes the Debye length, L_D, and, consequently, the "width" of the grain boundaries. The assumption of constants σ_2 and σ_1 along the boundary, or along the grain, does not correspond with actual conditions, except when L_D is many times smaller than the mean grain measurements. Change in induction, D, is associated with a bend in vector E at the passage through the boundary of the two media, and this was not taken into consideration in the above paper. In the case of the general solution, one should know the mathematical grain distribution in the polycrystalline specimen, as well as the dielectric constant (specific inductive capacity) of boundaries and grains. The appearance of energy barriers between grains also is possible. These barriers effect the temperature and luminescense relations of the Hall mobility and conductance, as well as the scattering of current carriers. In addition to the above stipulations, the discussion of the equations derived in Section 3 yields certain practical suggestions for the measurements of polycrystalline layers.

5. Discussion of results

5.1 Low-resistance boundaries, $\sigma_2 > \sigma_1$

In concordance with Section 3.2, measurement of a polycrystalline specimen will show the conductance to be higher than the conductance in grains (σ σ_1). The Hall voltage will be many times smaller ($V_H < V_{H1}$) than for a homogeneous specimen. Hall mobility will be less than in the grains, and the calculated concentration will be greater.

5.2 High-resistance boundaries, $\sigma_2 < \sigma_1$ /860

a) Boundaries parallel with the j_x vector.

The grain boundaries parallel to the current vector j_x influence the Hall voltage, V_H, but this influence is considerably smaller than that of the perpendicular boundaries.

Let us suppose that we have at our disposal a plate composed of large monocrystalline blocks of different orientation. If a Hall specimen cannot be cut from a single block, it should be done such that the boundaries run more or less parallel to the current flow. Furthermore, if the blocks in the specimen have the approximate parameters σ and μ, the measured Hall effect will have the same value as will a homogeneous specimen (see Eq. (6)). If $\mu_1 \neq \mu_2$ and $\sigma_1 \neq \sigma_2$, the measured voltage V_H across a polycrystalline specimen with parallel high-resistance boundaries will be lower than the Hall voltage across the grains themselves.

b) Boundaries perpendicular to the j_x vector.

The effect of grain boundaries perpendicular to the current vector, j_x, was calculated through Eq. (3) and (9), assuming σ_2 = const. σ_1 changes over a wide range from $\sigma_1 = \sigma_2$ to $\sigma_1 = 200\,\sigma_2$, for example, as a result of illumination of the specimen

Table 1

σ_1	σ "narrow" bound. $\frac{w}{h}=10$	σ "wider" bound. $\frac{w}{h}=2$
$\sigma_1=\sigma_2$	σ_1	σ_1
$\sigma_1=2\sigma_2$	$0{,}88\sigma_1$	$0{,}66\sigma_1$
$\sigma_1=10\sigma_2$	$0{,}509\sigma_1$	$0{,}2\sigma_1$
$\sigma_1=100\sigma_2$	$0{,}092\sigma_1$	$0{,}023\sigma_1$
$\sigma_1=200\sigma_2$	$0{,}05\sigma_1$	$0{,}01\sigma_1$

If grain conductance increases, the resultant conductance σ of the specimen increases, but at a slower rate because it is limited by the weak conductance of the grain boundaries.

The Hall voltage, V_H, as well as the Hall mobility, then is calculated assuming $\mu_1 = \mu_2$.

Table 2

Assuming $\mu_1 = \mu_2$

σ_1	V_H $\frac{w}{h}=10$	V_H $\frac{w}{h}=2$	μ $\frac{w}{h}=10$	μ $\frac{w}{h}=2$
$\sigma_1=\sigma_2$	V_{H1}	V_{H1}	μ_1	μ_1
$\sigma_1=2\sigma_2$	$1{,}09V_{H1}$	$1{,}33V_{H1}$	$0{,}959\mu_1$	$0{,}878\mu_1$
$\sigma_1=10\sigma_2$	$1{,}818V_{H1}$	$4V_{H1}$	$0{,}925\mu_1$	$0{,}8\mu_1$
$\sigma_1=100\sigma_2$	$10V_{H1}$	$34V_{H1}$	$0{,}92\mu_1$	$0{,}782\mu_1$
$\sigma_1=200\sigma_2$	$19V_{H1}$	$67{,}3V_{H1}$	$0{,}95\mu_1$	$0{,}673\mu_1$

If $\mu_1 \cong \mu_2$, the measured Hall voltage, V_H, is higher across very large boundaries, than the Hall voltage across the grains themselves, the lower the conductivity of the boundaries, and the greater their width. This proves that the entire Hall effect depends primarily on high-resistance boundaries. /861

Measured mobility, μ, differs little from the mobilities of grains and boundaries.

Table 3 lists voltage V_H and mobility μ for the case when $\mu_1 \neq \mu_2$.

If $\mu_2 < \mu_1$, measured mobility μ is always smaller than mobility μ, in the grains. The greater is this decrease the higher the resistance of the boundaries, and the greater their width.

Table 3

When $\mu_1 \neq \mu_2$

σ_1	μ_1	$\frac{w}{h}=10$	$\frac{w}{h}=2$	$\frac{w}{h}=10$	$\frac{w}{h}=2$
		V_H	V_H	μ	μ
$\sigma_1=\sigma_2$	$\mu_1=20\sigma_2$	$0{,}915V_{H1}$	$0{,}683V_{H1}$	$0{,}915\mu_1$	$0{,}683\mu_1$
$\sigma_1=2\sigma_2$	$\mu_1=20\mu_2$	$0{,}92V_{H1}$	$0{,}7V_{H1}$	$0{,}809\mu_1$	$0{,}462\mu_1$
$\sigma_1=10\sigma_2$	$\mu_1=20\mu_2$	$0{,}95V_{H1}$	$0{,}833V_{H1}$	$0{,}483\mu_1$	$0{,}166\mu_1$
$\sigma_1 \doteq 100\sigma_2$	$\mu_1=20\mu_2$	$1{,}46V_{H1}$	$2{,}3V_{H1}$	$0{,}134\mu_1$	$0{,}0529\mu_1$
$\sigma_1=200\sigma_2$	$\mu_1=20\mu_2$	$1{,}82V_{H1}$	$4V_{H1}$	$0{,}091\mu_1$	$0{,}04\mu_1$

Let us illuminate a polycrystalline specimen. Let us assume σ_1 changes from $\sigma_1 = 2\sigma_2$ to $\sigma_1 = 100\sigma_2$, and that the width of the grain boundaries is from $h = w/2$ to $h = w/10$. Table 3 shows that this illumination produces an increase in measured mobility, μ, by a factor q15.

6. Hall effect measurements in cadmium selenide vapor-grown layers

Some properties of vapor-grown CdSe layers can be explained by using the above model of a polycrystalline layer. Included among others is the relationship between Hall mobility and light. This mobility shows certain characteristics that persuaded the authors to examine this question.

Light causes a change in the filling of dispersion and recombination centers of semiconductors of the CdSe type that can result in a threefold change in mobility attributable to light [2]. On the other hand, an increase by a factor of 30 is observed in mobility, μ, in polycrystalline layers when the specimen is illuminated [3].

The effect of light on change in mobility was found, upon examination, to depend on the treatment given the layers. Typical results are listed in Table 4. These results can be summed up as follows. Unwarmed specimens, or those warmed in air at temperatures below 400°C, show an increase in mobility upon illumination. Table 3 shows that this happens with increase in σ_1, and with decrease in h, and $\mu_2 < \mu_1$. Atmospheric oxygen probably diffuses from the grain boundaries into the depth, forming acceptor conditions. Partial oxidation of CdSe to $CdSeO_3$ also is possible. If this is so, conductance σ_2 of the boundary will decrease, and inflection of the CdSe energy bands will develop at the boundary. Illumination increases σ_1, and decreases the Debye length at the boundaries. Boundary width, h, decreases.

Specimens, warmed to 400°C in air, or in argon, show a drop in resistance, /862 and oxygen is released from the layer. The boundaries that develop are characterized by small μ_2 and σ_2, as well as by constant h.

Table 4

No.	Treatment	$\rho \cdot 10^2$ dark [Ω·m]	$\mu \cdot 10^4$ dark [m²/Vs]	$\mu \cdot 10^4$ bright 5000 lux [m²/Vs]	Remarks
1		$5 \cdot 10^3$	40	120	Increase in grain conductance with light, decrease in boundary width.
2	1 hour warming in air at 400°C	$2 \cdot 10^3$	100	15	Boundaries of constant width, displacement of O_2 from bound.
3	1 hour warming in argon at 400°C	$9 \cdot 10^2$	60	35	Boundaries of constant width, displacement of O_2 from bound.
4	Warming at 250°C in air	$6 \cdot 10^4$	10	70	Increase in grain conductance with light, decrease in boundary width.
5	With a 10 nm indium vapor-grown layer on top	$5 \cdot 10^{-1}$	10	10	Increase in conductance of boundaries, slight increase in conductance of grains, decrease in mobility
5a	Same specimen (#5) warmed in argon at 300°C	$2 \cdot 10^{-1}$	0,5	0,5	

The width of the boundary does not depend upon illumination. Measured μ decreases with increase in σ_1, as will be seen from Table 3.

The results for specimen No. 5 concord well with the model with high σ_2 boundaries. After warming the CdSe specimen with vapor-grown indium in argon, conductivity increased (by a factor of 2.5-fold), and mobility decreased by a factor of 20.

This can be interpreted as suggesting that the indium diffuses more rapidly in a region with an imperfect lattice, i.e., boundaries, than in grains. Indium is a donor admixture for CdSe. When it diffuses into the boundaries, it reacts frequently with oxygen, forming relatively good conducting oxides.

As we see, interpretation of the results of Hall measurements, and of conductivity of polycrystalline specimens, is very difficult. Generally speaking, the differences between parameters σ, μ, and R_H for the grains, as well as for specimens as a whole, can differ by orders of magnitude. Further discussion of the influence of grain boundaries on measurements is welcome.

Summary

A model of a polycrystalline semiconductor is presented. It is assumed that the grains and the grain boundaries have different conductivities and different Hall mobilities. The effect of the grain boundaries on the values of measured conductivities, of Hall mobility, and of carrier concentration is estimated. The model is used to explain the relationship of mobility to illumination of a polycrystalline cadmium selenide test specimen and its dependence on the conditions under which the above-mentioned layers are obtained.

REFERENCES

1. Kobus, A., Tuszynski, J., Hall Trons and Their Application, WNT, Warsaw, 1963.

2. Bubo, R. H., Donald, H. E., Blanc, I., "Photo-Hall Effects in Photoconductors," J. Phys. Chem. Solids, 1961, 22:173-180.

3. Fowler, A. B., "Photo-Hall Effects in CdSe Sintered Photoconductors," Ibid., p. 181-188.

Translated for the National Aeronautics and Space Administration under contract NASw-2038 by Translatiȯn Consultants, Ltd., Arlington, Virginia.